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Review of Chlorine and
Organohalides and Their
Significance to
The Royal Australian Navy

F. John Upsher and
Lyn E. Fletcher

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F. John Upsher and Lyn E. Fletcher

**Ship Structures and Materials Division
Aeronautical and Maritime Research Laboratory**

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ABSTRACT

There is increasing global disquiet about the concentration of chlorine compounds found in the natural environment. When chlorine is mixed with ship sewage up to 10% of applied chlorine can be converted to organohalides. Chlorine and residual oxidants are readily dissipated and their environmental effects are of lesser significance than the potential toxicity of the organohalides. Organohalides readily bio-accumulate and are persistent in the environment. Their presence has been associated with tumours and cancers, birth defects, interference with reproduction and behavioural problems. These effects are greatest in animals at the end of the food chain, including sea birds, whales and dolphins.

The Royal Australian Navy (RAN) is currently chlorinating ship sewage on some ships prior to discharge. This review was undertaken to assess whether this could pose an unacceptable environmental risk and subsequently be subject to future regulation. It is concluded that chlorinating sewage may pose an environmental risk, however, the level of that risk is unclear. In addition, it is conceivable that further regulation may occur. Moreover, the OMNIPURE units in use by the RAN are not effectively meeting the International Maritime Organisation's regulations for sewage discharge at present. Consequently, it is advisable that alternative sewage treatment systems be adopted.

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Executive Summary

Chlorine is currently in widespread use as a disinfecting and oxidising agent. Over 20 ships of the Royal Australian Navy (RAN) currently use OMNIPURE units to chlorinate ships sewage, to meet International Maritime Organisation (IMO) guidelines for the biochemical oxygen demand (BOD₅), faecal coliforms and total suspended solids requirements for the effluent. However, chlorine and its reaction products have been identified as being toxic to many marine species. Consequently, pressure is mounting to reduce or eliminate chlorine use. A new Defence Instruction Navy (DI(N) OPS 19-1) has been written which voluntarily restricts residual chlorine discharge from RAN ships to an average of 20 mg/l.

This report reviews the relevant literature and uses trial data from HMAS Hobart's OMNIPURE plants to determine if chlorinating sewage on RAN ships is causing or adding to existing environmental problems. This report also assesses the suitability of the DI(N) limit of 20 mg/l residual chlorine.

Chlorinating ship sewage in the presence of seawater produces a range of reaction products including a number of reactive and oxidizing inorganic chlorine compounds. Reaction of these compounds with organic substances yield a variety of organohalides. All of these substances are toxic to a variety of marine species and this toxicity is frequently observed at concentrations in the mg/l range. Many organohalides have been shown to cause cancer and birth defects. Toxic effects are most pronounced in small species and in the young of larger species. Organohalides are persistent in the marine environment and are capable of being ingested by marine species and will bioaccumulate up the food chain, where the concentrations of these chemicals are magnified in species such as whales, seals, sea birds and man.

The OMNIPURE units on HMAS Hobart produced effluents with an average residual chlorine concentration of 50 mg/l. Trihalomethanes concentrations were around 0.1 to 0.2 mg/l and the total organohalide concentration was estimated to be up to 2.3 mg/l. At these levels, OMNIPURE effluents can be expected to cause localised disturbances due to high residual chlorine levels. However, rapid dilution will significantly reduce this disturbance. The trihalomethanes and other organohalides produced will add to the load of organohalides already present in the marine environment where they will add to a growing environmental problem. The exact extent of this impact is difficult to predict but the political and regulatory pressure on chlorine use and discharge is expected to increase. The US Navy has seen their use of chlorine for sanitation restricted in Pearl Harbour where US Navy ships are not permitted to discharge more than 0.1 mg/l residual chlorine for 2 hours/day. HMAS Hobart's OMNIPURE sewage effluent is approximately 500 times this concentration. Consequently, increased

political and regulatory pressure may in future impinge on RAN operations if chlorine use continues.

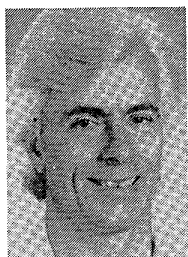
The OMNIPURE units on HMAS Hobart were found to be meeting neither the DI(N) for residual chlorine nor the IMO standards. It is also unlikely that these units can be made to meet both requirements concurrently. However, the IMO regulations are international law and at present, residual chlorine discharge is not regulated internationally. Therefore, the IMO regulations should take priority. To achieve this, it would be necessary to increase the effluent chlorine levels. This is in conflict with the RAN's commitment to voluntarily reduce residual chlorine discharges.

Consequently, it is recommended that RAN moves away from the process of chlorinating ship sewage. In the interim, to reduce the environmental impact of discharging OMNIPURE effluent, this discharge should be limited to areas away from breeding grounds, entrances to estuaries and the Great Barrier Reef Region. To facilitate this, DI(N) OPS 19-1 would require amendment.

Authors

F. John Upsher

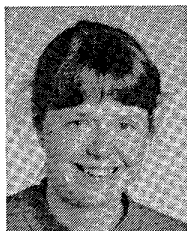
Ship Structures and Materials Division



John Upsher, BSc Hons (Bath), MSc (La Trobe), joined Materials Research Laboratory as a microbiologist in 1966 then for 20 years investigated different problems associated with microbial deterioration of materials and equipment in storage and in the tropical environment. Responding to increasing concern within Defence on environmental matters, he has more recently investigated the bacterial generation of hydrogen sulfide in naval oily water wastes and the disposal of wastes including sewage and plastics.

Lyn E. Fletcher

Ship Structures and Materials Division



Lyn Fletcher, BAppSc (Chem.) (RMIT) joined Materials Research Laboratory in 1985 and worked for three years on research into polymer and solvent interactions. She then joined a small multidisciplinary group investigating some environmental problems encountered by the Royal Australian Navy. In support of this work, Lyn is currently studying for a MEnvSc at Monash University.

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1. Introduction

Chlorine is a powerful oxidant and chlorination has become entrenched as an industrial process where rapid oxidation is required. It is commonly used to decolourise materials such as paper pulp and water and to reduce the organic content, and to sanitise sewage, water supplies and contaminated waters. The greater part of the chlorine is reduced to chloride but a portion comes to reside in a variety of chlorine substituted organic molecules.

When chlorination became the standard method to decolourise and to sanitise water supplies, off-flavours were immediately detected. These were identified as chlorophenols that resulted from chlorination of phenolic substrates. When more systematic studies were made of chlorinated waters in America, the analytical methods that were available at that time favoured the detection and estimation of the smaller, volatile organochlorides. Since the seventies, several investigations have indicated a great array of organochlorides in chlorinated water supplies (Bellar *et al.*, 1974; Kraybill, 1978; Rook, 1974).

These compounds are potentially toxic to humans through ingestion. Several surveys in the USA showed elevated incidences of cancer, especially of the bowel and bladder, occurring in areas where the potable water supply was the product of repeated chlorination and carried a high organochloride burden (Cantor and McCabe, 1978; Salg 1978; Shy and Struba, 1980).

Further research observed toxicological effects in other species caused from other chlorination processes. Industries using most chlorine received greatest attention and the paper pulp bleaching process in particular was critically examined. Chlorination of water supplies and recreational waters remain a major decolourisation and sanitisation process and alternative oxidative processes are being introduced. Chlorination remains a preferred process for treating sewage and municipal liquid waste where it has to be sanitised, largely because it is reasonably cheap and efficient in achieving the desired effect.

Sewage chlorination installations are fitted on over twenty Royal Australian Navy (RAN) ships, including those of the DDG class. The chlorination is performed with OMNIPURE units which electrolytically produce chlorine from the chloride ion present in seawater. The chlorinated sewage is then reacted for 30 minutes before being discharged into the ocean. It is RAN policy that current OMNIPURE equipment will continue to be employed until those ships are decommissioned but that no more sewage chlorination equipment is to be purchased. Alternative systems under consideration include collection, holding and transfer tanks (CHT) and biological units. Factors of reliability, efficiency and maintenance were contributory factors to that decision rather than environmental concerns.

In 1994, a Defence Instruction (Navy), *DI(N) OPS 19-1 Policy for the Disposal of Shipborne Waste* (Department of Defence, (Navy) 1994) was issued to address this matter in advance of any applied legislation. Section 19 *Sewage (Blackwater) Policy* defines that:

a. *New ships shall have the self-contained means of safely being able to:*

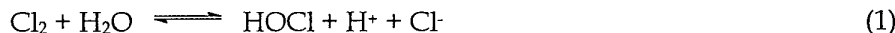
3. *keep discharge levels of chlorine from any fitted sanitation device below a geometric mean of 20ppm whilst in operation.'*

This review will, by examining all aspects of the environmental impact of chlorine, assess the relevance of that arbitrary limit and consider the advisability of continuing to use OMNIPURE units to chlorinate sewage on HMA Ships.

2. The Chemistry of Chlorination

2.1 Chlorine in Water

Chlorine gas (Cl_2) when added to water readily hydrolyses producing hypochlorous acid by reaction 1.

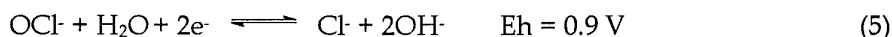


The equilibrium constant for this reaction is $1.5\text{-}4 \times 10^{-4} \text{ (mol/l)}^2$ (Jolley & Carpenter, 1983) for temperatures ranging from 0-25 °C. This reaction is also rapid. For example at pH greater than 6 and at temperatures above 1°C, the hydrolysis is virtually complete in under one second (Singer *et al.*, 1988). Hydrolysis of chlorine will also result in a lowering of the pH because of hydrogen ion production. In addition, hypochlorous acid is weak acid which will dissociate.



The pKa value for this reaction is 7.53 at 18°C. Consequently, at pH above 7.5, OCl^- dominates and at pH below 7.5, HOCl dominates.

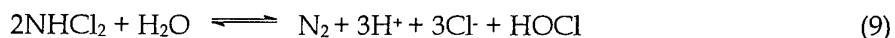
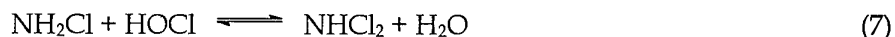
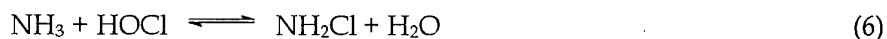
Consequently, three oxidising compounds are present: Cl_2 , HOCl and OCl^- . Each of these is capable of oxidising organic materials and disinfecting water. However, HOCl is the most powerful oxidant and is the form responsible for most oxidation reactions in water. The other forms may be involved directly to a lesser extent but importantly they form a reservoir capable of producing additional HOCl until all three chemical forms are exhausted. The half-cell reaction and electrochemical potentials for these compounds are shown in equations 3-5. All of these chemical compounds are measured as free available chlorine.



2.2 Chlorine in Sewage

2.2.1 Reaction with nitrogen compounds

When free available chlorine comes in contact with ammonia or organic amines in water additional reactions can occur. These occur because chlorine in hypochlorous acid (HOCl) can substitute for hydrogen in ammonia. These reactions are important in sewage treatment since ammonia is frequently found in high concentrations. The common reactions that occur between free chlorine and ammonia are shown in the following equations.



These reactions do not necessarily occur in a step-wise fashion and are pH sensitive. When the chlorine to ammonia molar ratio is equal to or less than 1 (or 5:1 by weight) essentially all of the free chlorine will be converted to monochloramine (equation 6). The rate is pH sensitive and is most rapid at pH 8.3. Increasing the chlorine to ammonia ratio to between 1 to 1.5 causes dichloramine to form. Dichloramine formation is enhanced at lower pHs. However, dichloramine is unstable and will rapidly decompose as in equation 9. For nitrogen trichloride formation a pH below 7.5 is required, with a chlorine to ammonia ratio of about 3. At higher pH, dichloramine is less stable and reaction 9 will proceed so quickly that equation 8 will not be observed. Nitrogen trichloride is also unstable in water and will decompose (Singer *et al.*, 1988). In practice, at a chlorine to ammonia ratio of 1.5, most of the original ammonia is converted to nitrogen gas.

The result of this chemistry is that addition of chlorine to waters containing ammonia will result in different amounts of free and combined chlorine being present. The relative amounts of free available chlorine and combined chlorine are not linearly dependent and produce the so called "breakpoint" phenomenon as shown in Figure 2.1.

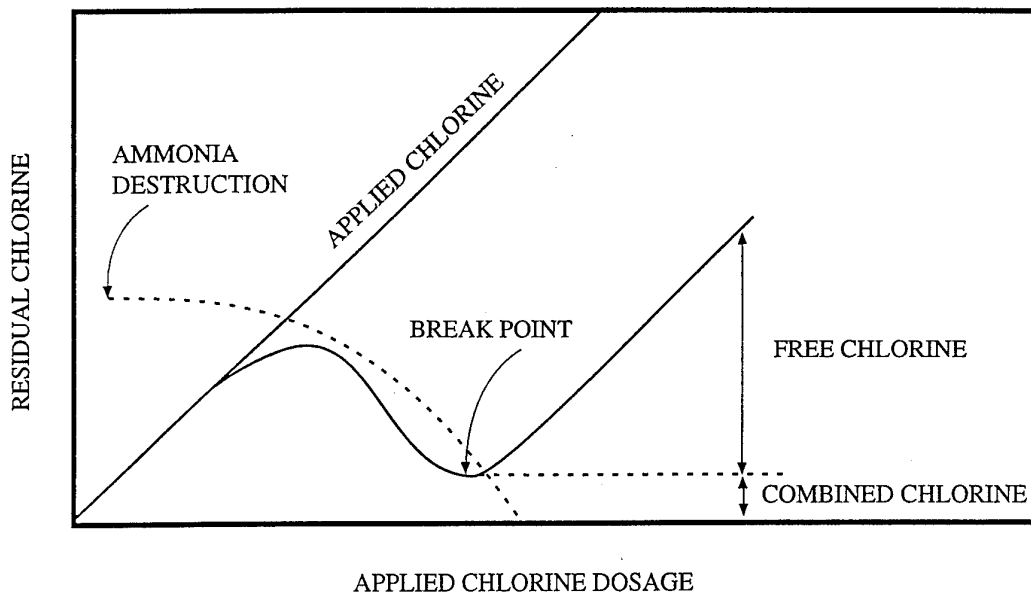


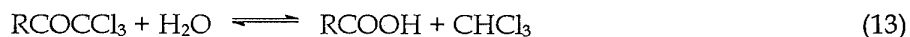
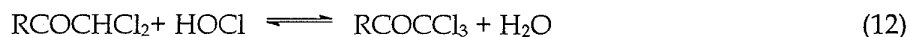
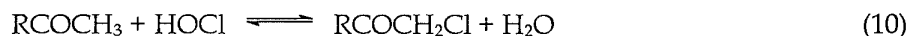
Figure 2.1. Graphic description of the break point phenomenon. (Jolley and Carpenter, 1983).

When chlorine is initially added and the chlorine to ammonia ratio is less than 1, the HOCl is rapidly converted to monochloramine. During this phase monochloramine is the major compound present. At a chlorine to ammonia ratio of around 1 the combined chlorine concentration is at its greatest. Adding further chlorine results in the formation of dichloramine which is unstable and will decompose, producing nitrogen and converting the chlorine to chloride. This results in the observed reduction of combined chlorine concentration until a minimum is reached which is called the break point. This break point is usually observed at a chlorine to ammonia ratio of around 1.65 (Jolley and Carpenter, 1983). If more chlorine is added after the break point it will be present as free chlorine since all available ammonia has been exhausted. The residual chlorine, measured after the break point, will consist of both free and combined chlorine. If the chlorine to ammonia ratio is less than the breakpoint then the residual chlorine concentration will consist entirely of combined chlorine.

Chloramines possess some germicidal activity. Monochloramine, the major chloramine present, is a less effective germicide than HOCl by a factor of approx 10^4 (Jolley & Carpenter, 1983). However, monochloramine is in equilibrium with HOCl, as in equation 6, but the concentration of HOCl will be much reduced. Similar reactions also occur with organic amines to produce organic chloramines. These compounds are still measured in the combined chlorine analysis but have much reduced germicidal power (Singer *et al.*, 1988). The presence of organic amines can therefore have a large impact on the chlorine required to effectively disinfect sewage and can leave a large residual chlorine level, since these will not decompose to nitrogen. In addition, small amounts of nitrates have been observed, formed by the oxidation of ammonia by HOCl (Blatchley, 1993).

2.2.2 Reaction with organic compounds

The amount of organic material present is usually measured as the total organic carbon (TOC) or as the amount of oxidisable material present which can be measured either as the chemical oxygen demand (COD) or the biochemical oxygen demand (BOD₅). Chlorinating sewage lowers all of these concentrations mostly through simple oxidation reactions which accounts for about 90% of the added chlorine (Rook, 1974). Around 6-10% of the free chlorine is involved in substitution reactions with organics to form a variety of volatile and non-volatile organohalides. A major product group is the trihalomethanes (THM), of which chloroform is a typical member. These are produced according to reactions 10-13 from methyl ketones or compounds oxidisable to methyl ketone.



Trihalomethanes are toxic and high levels of these compounds are a major disadvantage of chlorination. Most sewage does not contain enough methyl ketones to account for the level of halomethanes produced (Morris, 1978) and other organic compounds including some large, naturally occurring molecules such as humic acid are also involved in this reaction (Rook, 1974, Morris and Baum 1978). Proteins are also present in sewage and natural waters and have been found to be precursors of THM (Scully *et al.*, 1985).

More toxic compounds can be produced by substitution reactions with aromatic compounds. For example phenol and benzoic acids which have been activated by the presence of another functional group on the aromatic ring can react with free chlorine to produce a variety of chlorophenols and chlorobenzoic acids (Rockwell and Larson, 1978). Free chlorine reacts with p-hydroxybenzoic acid more readily than does monochloroamine, a component of combined chlorine.

Lipids and fatty acids are commonly present in sewage. Fatty acids are unsaturated organic acids having at least one double bond where addition of free chlorine can occur. Chlorination of oleic acid with HOCl at a 1.5 molar ratio resulted in more than 10% of the added chlorine being incorporated into this compound in one hour. The major identified chlorinated product was 9-chloro-10-hydroxy methyl stearate. Other fatty acids varied in the amount of chlorine incorporated with in the range 1.67-29.1% (Ghanbari *et al.*, 1983).

In sewage treatment, the variety of possible reactants and of chlorinated products from the substitution and addition with free chlorine is immense. One early study identified over 50 chlorination products in municipal wastewater, (Glaze & Henderson, 1975) and some are listed in Table 2.1. Many of those identified are aromatic and were present in the 'µg/l' or ppb range, when chlorine was added in a large dose (2000-4000 mg/l).

Table 2.1. Halogenated organic compounds observed after sewage effluent chlorination (Glaze and Henderson, 1975)

Compound	Concentration (µg/l)
Chloroform	
Dichlorobromomethane	
Dichlorobutane	27
3-chloro-2-methylbut-1-ene	285
Chlorocyclohexane	20
Chloroalkylacetate	
o-dichlorobenzene	10
Tetrachloroacetone	11
p-dichlorobenzene	10
Chloroethylbenzene	21
Pentachloroacetone	30
Hexachloroacetone	30
Trichlorobenzene	
Dichloroethylbenzene	20
Chlorocumene	
N-methyl-trichloroaniline	10
Dichlorotoluene	
Trichlorophenol	
Chloro-α- methylbenzylalcohol	
Dichloromethoxytoluene	32
Trichloromethylstyrene	10
Trichloroethylbenzene	12
Dichloro-bis(ethoxy)benzene	30
Dichloro-α-methylbenzylalcohol	10
Trichloro-N-methylanisole	
Trichloro-α-methylbenzylalcohol	25
Tetrachlorophenol	30
Trichlorocumene	
Tetrachloroethylstyrene	
Trichlorodimethoxybenzene	
Tetrachloromethoxytoluene	40

In addition to the above list, other organochlorides have been identified when different wastewaters and organic materials are chlorinated. These compounds are listed in Table 2.2.

Table 2.2. Additional Organochloride Compounds Produced During Chlorination of Organic Material.

Compound	Reference
Trichloroacetaldehyde	Norwood <i>et al.</i> (1984)
Methyl-1-chloroacetate	Norwood <i>et al.</i> (1984)
Methyl- 1,1-dichloroacetate	Norwood <i>et al.</i> (1984)
Methyl-2,2-dichloropropionate	Norwood <i>et al.</i> (1984)
Methyl-3,3-dichlorobutanoate	Norwood <i>et al.</i> (1984)
numerous chlorinated methyl diesters	Norwood <i>et al.</i> (1984)
5-chlorouracil	Kopperman <i>et al.</i> (1975)
5-chlorouridine	Kopperman <i>et al.</i> (1975)
8-chlorocaffeine	Kopperman <i>et al.</i> (1975)
6-chloroguanine	Kopperman <i>et al.</i> (1975)
8-chloroxanthine	Kopperman <i>et al.</i> (1975)
2-benzoic acid	Kopperman <i>et al.</i> (1975)
5-chlorosalicylic acid	Kopperman <i>et al.</i> (1975)
5-chloromandelic acid	Kopperman <i>et al.</i> (1975)
2-chlorophenol	Kopperman <i>et al.</i> (1975)
4-chlorophenylacetic acid	Kopperman <i>et al.</i> (1975)
4-chlorobenzoic acid	Kopperman <i>et al.</i> (1975)
4-chlorophenol	Kopperman <i>et al.</i> (1975)
3-chlorobenzoic acid	Kopperman <i>et al.</i> (1975)
3-chlorophenol	Kopperman <i>et al.</i> (1975)
4-chlororesorcinol	Kopperman <i>et al.</i> (1975)
3-chloro-4-hydroxybenzoic acid	Kopperman <i>et al.</i> (1975)
4-chloro-3-methyl-phenol	Kopperman <i>et al.</i> (1975)

Tables 2.1 and 2.2 illustrate the large range of organochlorine compounds that may be produced during the chlorination of sewage effluents. The broad categories of compounds include chlorinated aromatics, chlorinated aromatic acids, chlorinated acids and esters and chlorinated organic amines.

The chlorinated organics produced are often non-volatile and cannot be easily analysed by common analytical techniques. Consequently, these compounds are measured as total organic halogen (TOX).

The concentration of TOX produced has been found to be dependent on the concentration of organic carbon, initial chlorine dose and time. It follows the following relationship, where k_{TOX} is the reaction rate and α and β are parameters that can be evaluated for different substances and wastewaters (Urano & Takemasa, 1985).

Consequently the final concentration of organohalides is proportional to the initial chlorine dose, the concentration of organic material present in the waste and time.

$$[\text{TOX}] = k_{\text{TOX}}[\text{TOC}][\text{Cl}_2]^\alpha t^\beta$$

In addition to producing organohalides, the chlorine disinfection process produces non-halogenated organic compounds through simple oxidation. These products can also be mutagenic. One study of the non-volatile organics produced in the disinfection of waste water treatment plants identified a total of 106 non-halogenated organic compounds in the concentrates of controls and disinfected effluents. This study also demonstrated that while mutagenic organics can occur in waste water prior to disinfection, chlorination or ozonisation can lead to an increase in the total number mutagenic compounds in the effluent (Jolley *et al.*, 1983).

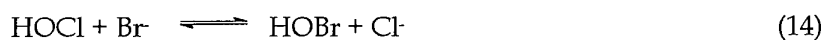
2.3 Reactions of Chlorine in Seawater and Sewage

Seawater contains many electrolytes that will react with free chlorine. Table 2.3 shows the average concentration of many important electrolytes.

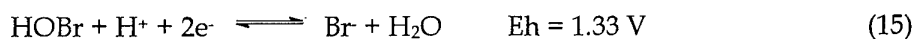
Table 2.3 *Electrolytes in seawater at a salinity of 3.5% (Riley & Skirrow, 1975)*

Electrolyte	Concentration (mg/l)
Cl ⁻	18,800
SO ₄ ²⁻	2,600
Br ⁻	65
F ⁻	13
HCO ₃ ⁻	140
Na ⁺	10,500
K ⁺	380
Mg ⁺⁺	1,350
Ca ⁺⁺	400

In the presence of Br⁻, HOCl is altered rapidly to HOBr, as in equation 14.



The electrochemical potential of HOBr is shown below.



The concentration of THMs produced in domestic waste water treatment plants can be related to the amount of oxidant present and the reaction time. Figure 2.2 illustrates this relationship where the amount of chlorine is related to the breakpoint number or

ratio of chlorine added to ammonia. When the ratio of chlorine to ammonia is high, more THMs are generally produced, except at around pH 5.

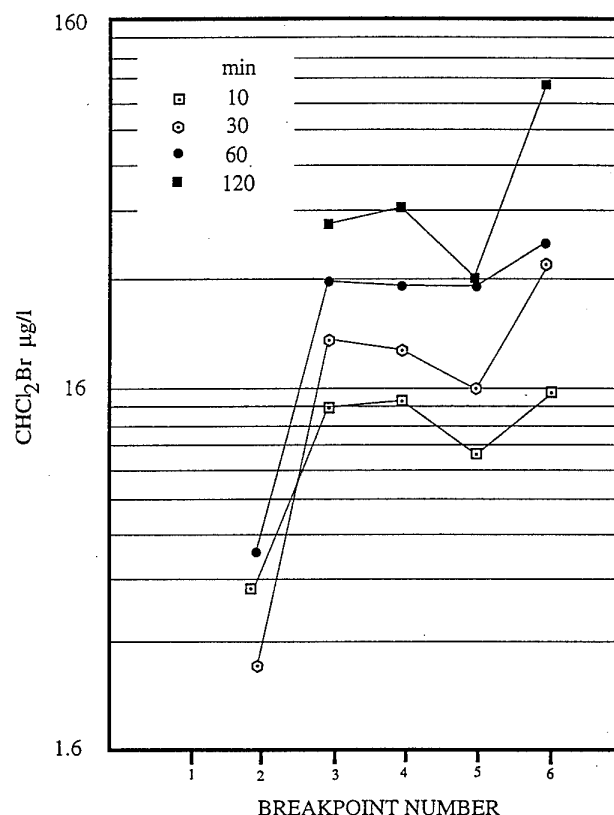
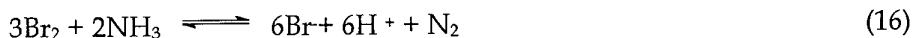


Figure 2.2 Effect of chlorine to ammonia ratio and time on THM formation in a waste water treatment plant (Cooper *et al.*, 1983).

HOBr is generally more reactive than HOCl for substitution reactions and the presence of HOBr will result in the formation of other trihalomethanes when HOBr substitutes for either one or all of the HOCl involved in the reaction sequences (equations 10-13). The additional trihalomethanes formed when Br is present are bromodichloromethane (CHCl_2Br), dibromochloromethane (CHClBr_2) and bromoform (CHBr_3). In the chlorination of seawater, the principle THM formed was bromoform, with dibromochloromethane and bromodichloromethane being formed in trace quantities but with no detectable chloroform (Bean *et al.*, 1978).

HOBr will also compete with HOCl when ammonia or organic amines are present, to produce bromamines. The chemistry of bromamine production is similar to the chloramine process (equations 6-9) except that dibromamine is more stable than dichloramine and dominates reactions under most conditions and with faster reaction rates (Jolley & Carpenter, 1983). The reactivity of chloramines and bromamines differ

substantially. In general bromamines are more oxidizing and less persistent than monochloroamine, the primary chloramine present in combined chlorine, and the toxicities are different (Inman and Johnson, 1978). The breakpoint reaction for bromine is shown by equation 16.



It is important to note here that most techniques to determine free chlorine and combined chlorine do not distinguish between chlorine and bromine but instead measure halogen contents (APHA, 1989). Consequently when bromide, free chlorine and ammonia are all present, various competing reactions will occur between bromide and ammonia for the free chlorine. Figure 2.3 shows the relationship between these three and the production of combined chlorine and bromine. It is also observed that the total residual oxidant concentration decreases with contact time and results in a flattening of the curves illustrated in Figure 2.3 (Fiquet, 1985). Consequently, the ammonia concentration of wastes will have a large impact on the reaction products from chlorination.

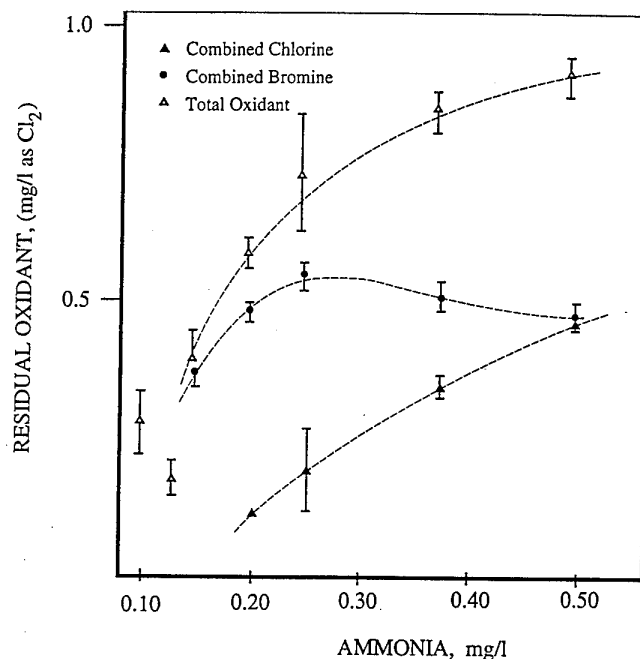


Figure 2.3 Residual oxidant concentrations in a seawater and ammonia system at 10 minutes is shown as a function of the original ammonia concentration. (Fiquet, 1985).

Like HOCl, HOBr is also involved in substitution and addition reactions to produce volatile and non-volatile brominated organics. Table 2.4 lists the major aromatic organobromides that have been identified from the chlorination of wastewaters in the presence of bromide ion.

Table 2.4. Organobromides identified following chlorination

Compound	Reference
bromodichlorophenol	Watanabe <i>et al.</i> (1984)
dibromochlorophenol	Watanabe <i>et al.</i> (1984)
2,4,6-tribromophenol	Watanabe <i>et al.</i> (1984)
bromotrimethylbenzene	Bean <i>et al.</i> (1978)
bromotetralin	Bean <i>et al.</i> (1978)
bromotetramethylbenzene	Bean <i>et al.</i> (1978)
bromonaphthalene	Bean <i>et al.</i> (1978)
bromomethylnaphthalenes	Bean <i>et al.</i> (1978)
bromobiphenyls	Bean <i>et al.</i> (1978)
bromodimethylnaphthalenes	Bean <i>et al.</i> (1978)
bromotrimethylnaphthalene	Bean <i>et al.</i> (1978)

Bieber and Trehy (1983) identified dihaloacetonitriles (DHAN) as major products from the chlorination of proteins. In the presence of seawater, the DHANs produced include dichloroacetonitrile, bromochloroacetonitrile and dibromoacetonitrile. This study also found that the formation of DHANs was dependent on the contact time and the residual chlorine concentration.

Another effect seawater may exert on the chlorination process is to contribute the alkaline cations, sodium and potassium. These can associate with free chlorine and bromine. It has been found that sodium or potassium hypochlorite increased virus inactivation at high pH and that sodium ions increased the rate of *Escherichia coli* inactivation by free chlorine (Haas and Brncich, 1985). This appears to be more important at high pH, where OCl^- would normally dominate and which has a lower oxidising potential than HOCl . It was suggested that NaOCl and KOCl have an efficiency closer to HOCl than to OCl^- (Haas and Zapkin, 1983).

3. Fate of residual oxidants and organohalides.

An understanding of the fate of residual oxidant and organohalides is important because in general, the greater persistence of chemicals in the environment, the greater will be the accumulated concentration and the greater the risk of toxic effects occurring. When chlorinated sewage is discharged into receiving waters residual oxidant, trihalomethanes and organohalides will be subjected to a variety of physical and chemical conditions that will eventually cause their degradation. The time required for degradation to occur varies substantially for different chemicals and the prevailing conditions.

The breakdown processes involved in the natural degradation of chlorinated chemicals include:

- biodegradation by the action of bacteria, algae and fungi
- biodegradation by internal enzyme systems of larger organisms
- photodegradation
- hydrolysis
- oxidation

Other physical processes will also reduce the concentration of the contaminant in water. They include:

- dilution and transport
- biotic assimilation
- adsorption on particulates and colloids
- volatilisation

3.1 Degradation of residual oxidants

Jolley and Carpenter (1983) reviewed the environmental fate of residual chlorine oxidants in receiving waters and proposed the scheme shown in Figure 3.1. All of the pathways indicated here can occur in sea water. Any free oxidant present will react initially with other reductants (Fe^{2+} , Mn^{2+} , NO_2^- , S^{2-} and HSO_3^-) in the receiving waters. In addition, hypochlorous acid will react rapidly with bromide ions present in seawater to produce hypobromous acid, which will decompose naturally to bromate as in equation 17. This reaction is accelerated in the presence of sunlight.



Other important reactions of free oxidants include oxidation of organic molecules resulting in conversion to chloride, substitution or addition reactions with organic or nitrogenous material present in the receiving waters (as in Chapter 2).

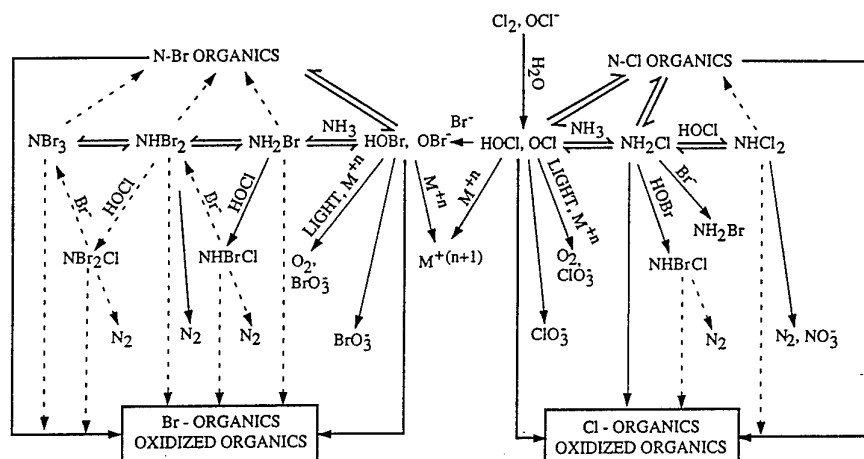


Figure 3.1. Principal chemical pathways for reaction, degradation and environmental fate of chlorine oxidants and organohalides in the aquatic environment. Presumed pathways, not yet proven, are indicated by dashed arrows.

Combined oxidant will be more persistent than free oxidant because of its reduced oxidation potential: its decay rate is approximately one tenth that of free oxidant. The decay pathway of combined oxidant is dependent on pH and the relative concentrations of oxidant, ammonia and bromide ion. Table 3.1 presents the results of a model scenario in which 0.8 mg/l of chlorine gas is added to artificial seawater at pH 8.2 with 0.4 mg/l ammonia (measured as nitrogen) and 0.01 mg/l organic amine (measured as nitrogen). It is observed here that organic amines are very rapidly converted to organic halamines, and that substitution is an important pathway for the decay of residual oxidant. (Jolley and Carpenter, 1983).

Table 3.1 Concentration of active halogen species in artificial seawater calculated with a kinetic model incorporating 21 chemical reactions (Jolley and Carpenter, 1983)

Time mins.	Free oxidant (mol/l)	Combined oxidant (mol/l)	Organic halamines (mol/l)	ammonia (mol/l)	organic amine (mol/l)
0	1.1×10^{-5}	0	0	7.1×10^{-7}	7.1×10^{-7}
1	3.6×10^{-6}	7.2×10^{-7}	7.2×10^{-7}	6.2×10^{-14}	0
10	1.5×10^{-6}	6.6×10^{-7}	7.2×10^{-7}	2.3×10^{-15}	0
30	6.7×10^{-7}	5.9×10^{-7}	7.2×10^{-7}	3.1×10^{-14}	0
60	3.7×10^{-7}	5.0×10^{-7}	7.2×10^{-7}	2.2×10^{-13}	0

The free oxidant in the above model mostly consisted of free bromine with an insignificant amount of free chlorine. This trend was repeated with the combined oxidant and organic halamines. Where most of the combined oxidant consisted of nearly equal amounts of the mixed bromochloramine and tribromamine, with about 10% bromamine, very low levels of chloramines were predicted. The majority of the organic halamines consisted of roughly equal amounts of organic N-substituted dibromides or mixed organic N-substituted chloride and bromide, again with very little organic N-substituted chlorides. Consequently, in seawater bromine-substituted organics and organic amines should dominate.

The major pathways for decay of combined oxidant will be the oxidation of organic and nitrogenous materials or substitution (Jolley and Carpenter 1983; Yamamoto and Fukushima 1992). Some of the discharged residual oxidant will be converted to further organic halides or organic chloramines.

3.2 Degradation of Organohalides

The same degradatory influences as listed for residual oxidants, above, will also be influential in dissipating organohalides in the sea but biodegradation will account for a greater portion.

The microbial capacity to degrade organohalides has been observed in most groups of microorganisms but is most consistently reported for bacteria. The abilities of

individual species vary considerably. A compound may be completely degraded and utilised as a nutrient or as an energy source (Dolfing and Harrison, 1992) or the event may be a serendipitous reaction of enzyme with a non-target substrate. Marine biodegradation can occur in either aerobic or anaerobic conditions, but the limited availability of nutrients is known to limit microbial activity.

Biodegradation is recorded for all significant types of organohalides (Trabalka, *et al.*, 1980; Shamat and Meier, 1980; Pearson and McConnell, 1975; Ghosal *et al.*, 1985). Degradation rates of aliphatic halides are generally increased with alkyl chain length. 1-Chlorodecane was degraded five times as quickly as 1-chloropropane (Gerhold & Malaney, 1966). Among the volatile aliphatic halides, most rapid degradation was observed for hexachloroethane, dichloromethane, bromochloromethane, tetrachloromethane, followed by 1,1-dichloroethane, trichloromethane, dichlorobromomethane, tribromomethane 1,1-dichloroethene, 1,1,2-trichloroethene, tetrachloroethene, 1,2-dichloropropane and 1,3-dichloropropene. Slowest to degrade were 1,1,2,2-tetrachloroethane, chlorodibromomethane, and trichlorofluoromethane (Tabak *et al.*, 1981). Ghisalba (1983) also found those latter compounds to be highly persistent in water. Increasing the number of chlorine atoms in alkanes, alkenes and aromatics usually decreases degradability but hexachloroethane and tetrachloromethane are exceptions.

In tracing the fate of three chlorinated hydrocarbons during four hours of biological wastewater treatment, Schröder (1987) assessed loss to air, adsorption on sludge, residue in effluent and biodegradation as shown in Table 3.2.

Table 3.2 Losses of organohalides in wastewater treatment (Schröder, 1987).

Compound	Waste air (%)	Sludge (%)	Effluent (%)	Degradation (%)
Trichloromethane	16	59	20	5
trichloroethane	17	58	18	7
hexachoro-1,3-butadiene	15	72	5	8

Biodegradation can occur in both aerobic and anaerobic conditions. Aerobic conditions persist in ocean waters, while both aerobic and anaerobic conditions will persist in the bottom sediments that can adsorb organohalide compounds. Reliable indications of degradability or the times required to achieve mineralisation or detoxification of most compounds are not known. However, an indication of the slowness can be gained from biodegradation values based largely on degradation rates determined for unacclimated river waters, as presented in Table 3.3. Degradation in the sea is not expected to be faster.

Photodegradation will also be effective in degrading organohalides in upper layers of ocean waters. The rate can be characterised by the time required to achieve a reduction in concentration of 50%, known as the half life. Table 3.3 lists the half lives for a

number of chlorination products. The photodegradation half lives are based on the degradation rate of direct photolysis of the compounds by sunlight in water.

Table 3.3. Degradation half lives of organochloride compounds, (Howard et al., 1991).

Chemical Compounds	Biodegradation (days)		Photodegradation (days)	
	High	Low	High	Low
pentachlorophenol	178	23	5	1 hour
2,3,4,6-tetrachlorophenol	168	28	14	1 hour
2,4,5-trichlorophenol	690	23	14	1 hour
2,4,6-trichlorophenol	70	7	4	2 hours
2,4-dichlorophenol	8.3	2.8	3 hours	0.8 hours
chloroform	180	28	Negligible	
bromoform	180	28	Negligible	
dibromochloromethane	180	28		
1,2-dichloroethylene	180	28		
1,3-dichloropropene	28	7		
chloroacetic acid	7	1	790	79

The THMs appear to be quite resistant to photolysis and slow to biodegrade but for these volatile compounds, volatilisation to the atmosphere could be a major means of loss from the receiving waters (Jolley and Carpenter, 1983).

Clearly, there are large variations in the environmental persistence of common organohalides. This range includes the variation between compounds and the variation shown for the same compounds for different conditions. In deep ocean waters it is proposed that losses by evaporation and photo-oxidation will be minimal because of limited access to the surface. Biodegradation will also be slow because of nutrient limitation to microbial activity. Thus, although it is not possible to accurately predict the persistence of individual organochlorine compounds it is expected that some organohalides will persist in receiving waters for a substantial time, with half lives greater than 6 months or more.

Physical dilution and transport processes will also effectively reduce the concentrations. Some of the organohalides produced are hydrophobic and will adsorb onto colloids and suspended solids. This will reduce organohalide concentrations in coastal waters, translocating them to sediments. They would then be less available for bioabsorption but could still enter the food chain through ingestion.

Consequently, given the slow natural degradation of some chlorination products, the addition of small quantities, as from treated sewage, could contribute to the accumulation of hazardous quantities, particularly in enclosed waters where mixing is restricted.

4. Biological Effects of Chlorine

4.1 Effects at the Cellular Level

In this section the term 'chlorine' is interpreted to include all of the residual halogen oxidants that arise when chlorine is mixed with water, sea-water or sewage and from reaction with bromide, ammonia and amino compounds. In the reports examined, there was no consistent effort to distinguish between the toxicity contribution by any individual components but it must be remembered that the presence of nitrogen compounds in reported test systems will have reduced the apparent toxicity.

In living systems most biochemical processes are affected and controlled by enzymes. These are protein molecules constructed so that their effectiveness is determined by the ability to 'fit' with a substrate molecule. Covalent or other bonds connect adjacent groups on the two molecules and site-specific bonding is made possible by favourable binding interaction energy between the active site and specific substrates. Thus, there are many sites in the enzyme/substrate arrangement where the placement of a specific reactant group is critical to the performance of a vital function (Jencks, 1975).

Thus any change in the molecular configuration of an enzyme molecule, such as chlorination of a double bond or substitution of groups such as hydroxyl, thiol or a terminal amino close to a critical site on either enzyme or substrate molecules, may prevent maximal interaction. Similarly changes in the localised binding energies result in reduced efficiency through effects like electrostatic repulsion and hydrogen bond breaking. Since most biochemical processes are potentially affected to similar degrees, cellular metabolism will be reduced cumulatively with the chlorine dose and with the duration of exposure.

Somewhat less sensitive to the molecular transformations caused by chlorine oxidants is the physical behaviour of cell walls and membranes. Cell walls in particular have evolved to their present forms in order to confer some resistance to outside influences and are thus able to accommodate a degree of molecular interference whilst retaining basic functions. This would be particularly so for free-living organisms and for the walls of the outer layer of cells (the epithelia) of macro-organisms. But since a basic function of the cell wall and membrane is to permit transmission of selected solutes, the relatively small OCl^- and HOCl moieties easily enter through slightly impaired membranes and are then free to react at the first available sites.

For any cell exposed to the influence of chlorine oxidants, there will be a degree of interference that can be tolerated without the effects being catastrophic. There would also be a proportion of sub-critical damage that could be overcome by repair mechanisms, after the oxidant is removed or exhausted. Mortality or non-viability of the cell or organism is then dependent upon the irreversible failure of the first vital function.

The action of free chlorine on virus particles has been reviewed by (Fujioka *et al.*, 1983). Free chlorine reacts with the outer protein coat on poliovirus and with internal ribonucleic acid (RNA) of bacterial f2 virus. However, after the chlorination of sewage, combined chlorine will generally be more abundant than free chlorine and will be the major inactivating agent. Monochloramine was shown to inactivate poliovirus by reacting with the protein coat so that the virus is unable to deliver its infective RNA into the host cell. However, monochloramine is much less effective than free chlorine and organic chloramines cause only minimal inactivation of poliovirus (Fujioka *et al.*, 1983).

4.2 Chlorine Damage to Animal Tissues

Assessment of the injury or trauma that is caused to living tissues by contact with an injurious substance is quantified against the concentration of the agent and the duration of exposure. Earliest indications of chlorine-induced damage are detected at the cellular level and manifested as a misfunction of a specific enzyme or of the cell membrane. Abnormalities are generally observed as leaking of an electrolyte or other substance. In whole macro-organisms these indications are less easy to determine than other, more gross signs of injury.

Studies on fish have shown that the first detectable damage is to blood cells. Osmoregulatory dysfunction, and disturbance to calcium and magnesium levels precede haemolysis (a disruption of the blood cells). These effects have been observed in a number of species (Hose *et al.* 1983, Cohen and Valenzuela, 1977, Middaugh *et al.* 1977, Buckley *et al.* 1976). Observable tissue damage to the gills is recognised as the 'classical' symptom of chlorine toxicity in fish. Typically there is separation of the respiratory epithelium, swelling and then haemorrhage of the gills (Hose *et al.*, 1983). This degree of damage has been reported to occur at a concentration of 0.1mg/l in 30 minutes (Hose *et al.*, 1983).

Further physiological changes following disruption of red blood cells (haemolysis) include liver, kidney and gill damage (Middaugh *et al.*, 1977, Bass and Heath, 1977). Membrane damage in the liver results in disruption of osmotic balance with loss of control of sodium, potassium and chloride ion flux. Damage to the kidneys results in failure to maintain ionic balance and the amino acid pool (Wiley, 1982). The levels of chlorine residuals causing those conditions are typically as low as 0.06 to 0.3 mg/l (Bass and Heath, 1977). Continued exposure to chlorine results in further deterioration of the gills with more dead tissue and loss of space between gill lamellae. Death is eventually caused by oxygen starvation (Wiley, 1982).

There may be partial recovery from sublethal chlorine induced trauma. In bluegill *Lepomis macrochirus* and rainbow trout *Salmo gairdneri* repaired gills are shortened with blunted lamellae and they contain irregular residual red blood corpuscle pools. However, vitality is greatly reduced (Bass and Heath, 1977).

Generally in fish, sensitivity to chlorine is reduced with increasing size which decreases the surface area to mass ratio. This pattern was observed in several species (Fobes, 1971, Hose *et al.*, 1983, Wolf *et al.*, 1975). Larvae of the striped bass were more sensitive than fingerlings (Brungs 1973). The blue crab *Callinectes sapidus* also showed this response (Laird & Roberts, 1980).

The long-term effects of chlorine on fish populations, and particularly on fish eggs, larvae and on reproductive behaviour, have received little attention but Arthur & Eaton (1971) found that spawning in the fathead minnow *Pimephales promelas* was reduced at 0.043 mg/l and eliminated at 0.085 mg/l.

Exposure of invertebrates to chlorine show generally similar effects to those seen in fish, with some showing greater sensitivity. Concentrations as low as 0.004mg/l (4ppb) for 96 hours at 26°C induces respiratory disruption and reduced growth in oyster *Crassostrea virginica* larvae, with reduced glycogen reserves in the adductor muscle in the adult (Scott and Middaugh, 1978). Concentrations less than 0.05 mg/l caused reduced pumping by the oyster (Scott & Middaugh 1978). Inhibition of shell growth in molluscs (Scott & Middaugh, 1978), failure of gametes to fertilise in three different invertebrates (Muchmore & Epel 1973) and failure of sessile molluscs to become attached (Khalanski & Bordet, 1980) have also been reported. Mussels appeared to be a little more tolerant than oysters. When adult mussels *Mytilus edulis* were exposed to chlorine levels between 0.2 and 5.0mg/l there was impaired muscular activity manifested by reduced pumping and feeding ability and reduced glycogen storage. There was also reduction in spat settlement, detachment of settled larvae and mortality of both larvae and adults (Khalanski & Bordet, 1980).

Scott & Middaugh (1978), examined the chronic effects of chlorine on oysters in all seasons and reached the general conclusions that concentrations in the range 0.6 - 1.2 mg/l were very toxic, resulting in severe effects including loss of shell substance. Concentrations in the range 0.11 - 0.21 mg/l were slightly toxic, inhibiting feeding and growth, increasing respiration and reducing reproductive potential.

The littleneck clam, *Protothaca staminea*, survived for up to eight months in chlorine concentrations of up to 0.1 mg/l but there was partial or complete inhibition of shell growth and generalised degradative tissue damage in the stomach, intestine and digestive tubules (Hillman *et al.*, 1980). Although adult crabs are considered to be somewhat more tolerant to chlorine than other species, when adult blue crabs *Callinectes sapidus* were exposed to levels of 0.27 to 1.04 mg/l of NaOCl, there was osmoregulatory stress as evidenced by elevated serum magnesium levels but respiration rates were not effected. Sensitivity to chlorine was determined to be inversely related to body weight (Laird and Roberts, 1980). Lobsters *Homarus americanus* exposed to 1mg/l of NaOCl for 60 minutes showed impaired respiration and subsequent reduced growth (Capuzzo, 1977)

4.3 Mortality Rates

The lethal effects of chlorine are commonly reported in terms of the LC_{50} which indicates the concentration of free chlorine residuals that when applied for a specified time causes the death of 50% of the test batch. This provides an index of a species ability to survive the effects of chlorine within the experimental population. Tests of this kind have been applied to a great diversity of marine animals, especially fish and invertebrates, including larval and immature forms. This information is summarised in Table 4.1 which is compiled from a number of sources and reinforces concerns over the toxicity of chlorine.

Table 4.1. *Lethal concentrations of chlorine for aquatic species.*

Species	Chlorine concentration (mg/l)	Criterion	Reference
Oyster larvae	0.6	48hr, LC_{50}	Roberts et al., 1975
White flounder	1.0	48hr, LC_{50}	Goldman, 1979
Common scup	1.2	48hr, LC_{50}	Goldman, 1979
Killifish	4.0	48hr LC_{50}	Goldman, 1979
Rotifers	1.2	48hr, LC_{50}	Goldman, 1979
Copepods	3.0	48hr, LC_{50}	Goldman, 1979
Lobster larvae	>5.0	48hr, LC_{50}	Goldman, 1979
Brook trout	0.04	48hr, LC_{50}	Dandy, 1977, in Brungs, 1973
Brook trout	0.08	7d, LC_{50}	Arthur, 1972, in Brungs, 1973
Brown trout	0.04	2min, LC_{100}	Pike, 1970, in Brungs, 1973
Rainbow trout	0.3	2hr, LC_{100}	Taylor et al., 1928, in Brungs, 1973
Rainbow trout	0.08	7d, LC_{50}	Merkens, 1958, in Brungs, 1973
Yellow perch	>0.88	1hr, LC_{50}	Arthur, 1972, in Brungs, 1973
Yellow perch	0.2	7d, LC_{50}	Arthur, 1972, in Brungs, 1973
Smallmouth bass	0.5	15hr, LC_{50}	Pyle, 1960 in Brungs 1973
Largemouth bass	0.36	12hr, LC_{50}	Arthur, 1972, in Brungs, 1973
Largemouth bass	0.26	7d, LC_{50}	Arthur, 1972, in Brungs, 1973
Fathead minnow	0.26	12h, LC_{50}	Arthur, 1972, in Brungs, 1973
Fathead minnow	0.1	96hr, LC_{50}	Zilich, 1969, in Brungs, 1973
Coho salmon	0.08	7d, LC_{50}	Holland, 1960, in Brungs, 1973
Pink salmon	0.1	2d, LC_{100}	Holland, 1960, in Brungs, 19734

5. Biological Effects of Organohalides

5.1 Bioaccumulation

The introduction of a chlorine atom into an organic molecule generally increases its solubility in fats which increases its ability to bioaccumulate and substantially alters its toxicity (Kopperman, 1976). Bioaccumulation of organohalides has been observed in all organisms examined, from plankton to mammals. Analysis of bottom dwelling organisms in the vicinity of an outfall of chlorinated sewage showed accumulation of short-chain halogenated hydrocarbons (Wharfe *et al.* 1981).

Experimental long-term administration of trihalomethanes, viz chloroform for fresh water fish and bromoform for seawater types, resulted in accumulation of those substances in the tissues, with consequent reduced growth and increased mortality (Anderson *et al.* 1978). The blue mussel *Mytilus edulis* and killifish *Oryzias latipes* showed considerable bio-concentration of 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene. It was also observed that levels subsided when external concentrations were lowered, particularly for THM (Saisho, 1994; Scott *et al.*, 1980).

The consequences of bioaccumulation are worst for those animals at the end of the food chain. Cetaceans (whales, dolphins, seals) and sea birds receive high concentrations of persistent organohalides arising from marine contamination. Tanabe (1994) reviewing mainly PCBs and chlorinated pesticides, confirmed bioaccumulation in the fatty tissue of marine mammals and noted quantities being passed to the next generation by suckling. Moreover, cetaceans have a low innate ability to metabolise these substances which compounds the problem. Analysis of wet fatty tissue from cetaceans in a worldwide survey showed PCB concentrations were highest in killer whales and were measured at over 100 µg/g. Other whale and seal species had PCB concentrations up to 80 µg/g. Concentrations increased with age, again demonstrating the accumulation process.

5.2 Toxicity of Organohalides

Trihalomethanes were shown to cause classical symptoms of toxicity when assayed with some fish cells, causing disruption of cell membranes, resulting in detectable cell leakage. There was also disruption to protein synthesis and increased cell mortality. Protein synthesis was the function generally disrupted first and at the lowest concentrations. Cell leakage followed, shortly preceding cell death. These observations are collated in Table 5.1. (Baksi, 1988).

Table 5.1. Toxicity of trihalomethanes to fish hepatocyte cells; concentrations at which there was significant reduction from the control response (Baksi, 1988).

Chemicals	Protein Synthesis (mg/l)	Cell Leakage (mg/l)	Cell Death (mg/l)
Chloroform	995	895	895
Dichlorobromomethane	410	820	820
Chlorodibromomethane	208	520	1040
Bromoform	253	506	506

In this study, bromoform was more than three times as toxic as chloroform, and so is a greater hazard for marine fish. (Baksi, 1988).

Organohalides were also observed to interfere with reproduction of fish and other marine organisms. 5-Chlorouracil and 4-bromoresorcinol, components of chlorinated municipal sewage, caused reductions to the rates of fish (carp) egg hatching (Gehrs *et al* 1974) and production of larvae by *Daphnia* at concentrations as low as 5-10 mg/l (Gehrs and Jolley 1978, cited in Trabalka and Burch, 1978).

Chlorinated phenols were considered to be the major cause of death in animals exposed to chlorinated sewage effluents. (Trabalka and Burch, 1978). Toxicity of chlorophenols and some other aromatics to *Daphnia pulex* at low concentrations are shown in Table 5.2.

Table 5.2. The 96-hour LC50 data for some chlorinated aromatics against *Daphnia pulex*.

Chemical	Concentration (mg/l)
2-chlorophenol	6.9
3-chlorophenol	5.6
4-chlorophenol	3.5
4-chloro-3-methylphenol	3.1
4-chlororesorcinol	1.0

As with chlorine and chlorine oxidants, smaller sized individuals, larvae and juveniles were more sensitive to organohalides than larger and adult forms (Scott, 1983).

Phytoplankton was also adversely affected by some organohalides. In particular 2,4,6-trichlorophenol, 2,4,6-tribromoanisole, pentachlorophenol and pentabromophenol were associated with inhibition of photosynthesis and cell division at concentrations between 0.5 and 1 mg/l but chloroform, bromoform, trichloroethylene, tetrachloroethylene ethylene bromide, 2,4,6-tribromophenol did not inhibit cell division in four different algae at concentrations up to 30mg/l (Erickson and Hawkins, 1980).

In ocean fish, organohalides have been linked to increased mortality, disease, breeding problems, malformations and behavioural disturbances. In whales, dolphins and seals they are associated with tumours and lesions, increased mortality, milk contamination, reproductive problems including sterility, immunological deficiencies, and developmental abnormalities (various sources cited in Ruchel, 1995).

5.3 Mutagenicity and Carcinogenicity of Organohalides

Mutagenic activity was found in effluents from paper pulp using chlorination and was attributed to the chlorinated organics present (Douglas et al., 1980). Kraybill *et al.* (1978) attributed increased incidence of bladder cancer with THM in water supplies. Later, mutagenicity was confirmed with cultured human and drosophila cells (Wilcox et al., 1988).

Refinement of analytical methods enabled the isolation and identification of the chemical species present in waters and wastes. Assessments for mutagenicity and carcinogenicity for some of these compounds are presented in Table 5.3.

Table 5.3. Mutagenicity of some organohalides

Chemical	Action	Reference
haloalkanes	carcinogenic	NCI, in Kraybill 1980
bromodichloromethane	mutagenic	Kraybill, 1980
dichloromethane	mutagenic	Kraybill, 1980
chloroform	carcinogen, hepatotoxic, nephrotoxic	Jorgenson et al., 1985
dichlorobromomethane	hepatotoxic, nephrotoxic	Condie <i>et al.</i> , 1983
dibromochloromethane	hepatotoxic, nephrotoxic	Condie <i>et al.</i> , 1983
bromoform	hepatotoxic, nephrotoxic	Condie <i>et al.</i> , 1983
tetrachloroethylene	mutagenic	Kraybill 1980
trichloroethylene	mutagenic	Kringstad <i>et al.</i> , 1983
1,2,3,4-tetrachloropropene	mutagenic	Rasanen <i>et al.</i> , 1977 cited in Rannug, 1980
haloacetonitriles		
dichloroacetonitrile,	mutagenic, genotoxic	Bull & Robinson, 1985
bromochloroacetonitrile	mutagenic, genotoxic	Bull & Robinson, 1985
dibromoacetonitrile	genotoxic	Bull & Robinson, 1985
haloacid derivatives		
dichloroacetic	carcinogenic, neurotoxic, ocular lesions	Stacpoole <i>et al.</i> 1979
chlorophenols		
2,4-dichlorophenol	foetotoxic, tumour promoter	Exon & Koller, 1985
2,4,6-trichlorophenol	carcinogenic	National Cancer Inst. 1979
halogenated p-cyrenes	mutagenic	Rasanen, 1977, cited in Rannug, 1980
chlorinated ketones, aldehydes		
1,1-dichloropropanone	mutagenic	Meier <i>et al.</i> , 1985
1,1,1-trichloropropanone	mutagenic	Meier <i>et al.</i> , 1985
chloropropenal	mutagenic	Kringstad 1983
monochloroacetaldehyde	mutagenic	Kringstad 1983
chloroacetones	mutagenic	Kringstad 1983
3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone	mutagenic	Kronberg <i>et al.</i> , 1988
E-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid	mutagenic	Kronberg <i>et al.</i> , 1988

Confirmed carcinogens and mutagens are therefore present, albeit in trace amounts. Consequently their long term potency is observed largely through epidemiological evidence. Kraybill (1978) associated the presence of THM in water with increased incidence of bladder cancer and Salg (cited in Cantor and McCabe, 1978) in a study in the Ohio river area, also found a positive association for water chlorination with rectal and bladder cancers. Alavanja *et al.* (1978), in New York State, also concluded that products of chlorination in the water was a factor linked to increased incidence of cancer mortalities.

Two powerful mutagens, 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone and its geometric isomer E-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid were detected and identified in the mutagenic fractions of chlorine-treated drinking water, (Kronberg et al. 1988).

Haloacetonitriles which are present in treated drinking water and wastes are genotoxic. They are not only mutagenic to *Salmonella* but can also induce tumours in skin and lungs of mice (Bull and Robinson, 1985).

In view of mutagenic and carcinogenic properties of some organohalides in waters, Shy and Struba (1980) advised on extreme caution in regard to permissible levels of chlorinated organics in drinking water. Kool et al. (1985) proposed some maximum acceptable levels in drinking and surface waters. These are presented in Table 5.4.

Table 5.4. Some proposed maximum permissible concentrations for specific organochlorides in drinking water and surface waters. (Kool et al., 1985)

Chemical	Concentration in Surface Waters (µg/l)	Concentration in Drinking Water (µg/l)
bis(2-chloroethyl) ether	0.01	0.03
bis(2-chloroisopropyl) ether	25	3
bromodichloromethane	2	55
chloroform	30	100
tetrachloromethane	4.2	0.7
1,2-dichloroethane	20	0.06

However, considering the possibility of mutagenic events occurring after prolonged contact with the products of water chlorination, it can not be asserted that there should be any approved threshold level for chlorinated organics in drinking water. Consideration of the hypothetical risks associated with mutagens in drinking water are based on an assumed human consumption of a nominal quantity per day, such as two litres (Foran, 1990). The impact of that degree of exposure cannot be extended to the risk to marine animals that are constantly exposed to the contaminant. External contact by the marine subjects would be some orders of magnitude greater so any arbitrary threshold levels should be adjusted accordingly.

An extension of the risk of marine contamination to humans is through the harvesting of seafood. The bioaccumulation is then taken a stage further and man is at the end of the food chain, receiving doses of previously bioaccumulated organohalides.

6. THE OMNIPURE SYSTEM

6.1 System Description

Over 20 HMA Ships are fitted with the OMNIPURE sewage treatment plants (Bayliss & Creedon, 1993). These plants work by electrolytically producing chlorine from the chloride ions present in seawater. Figure 6.1 illustrates the major system components. The amount of chloride ion present is critical to maintain good conductivity, for the formation of free chlorine and the efficient operation of the unit. In HMA Ships some of the chloride ion will be present because of the seawater flushing of the heads.

Sewage with a monitored portion of sea water is first added to a surge tank where they are mixed. The sewage then gets macerated and is passed through a 'book'-type electrocatalytic cell where chlorine is generated. The chlorinated sewage is then pumped into the effluent holding tank, allowing a contact time of thirty minutes or more for the disinfection and oxidation processes to proceed and for solids to settle. The treated effluent is then discharged overboard and the settled solids are returned to the surge tank.

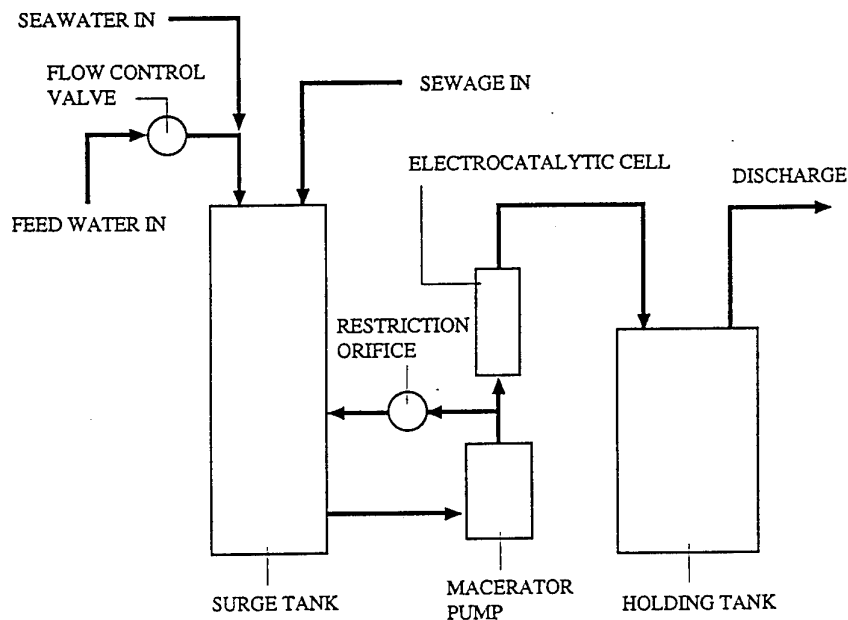
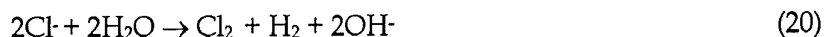


Figure 6.1 Major components of the Omnipure marine sanitation system. (Lardis & Brown, 1989)

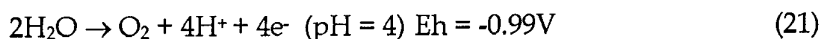
The 'book' type electrocatalytic cell consists of a series of bipolar titanium electrodes. The anodes and cathodes of each set are alternated along the length of the 'book'. When the 'book' is closed, pairs of alternate opposed anodes and cathodes are separated by a space, 0.64cm wide, through which the diluted, macerated sewage passes.

A current is set up through the cell and chloride is converted to chlorine by two main half cell reactions. The half cell reaction which occurs at the anode is shown in equation 16 and that which occurs at the cathode is shown in equation 17. The overall reaction in the cell is shown in equation 18. Applied current is between 0.04-0.064 A/cm² (Omnipure Technical Reference Bulletin).



The chlorine produced is rapidly hydrolysed to either hypochlorous acid or hypochlorite ion depending on the pH in the cell. Free chlorine can then undergo all of the reactions outlined in section 2. In particular, hypochlorous acid will be converted to hypobromous acid and free bromine and free chlorine will react with any ammonia in the sewage to produce chloramines and bromamines. Various organochlorides and organobromides will also be produced.

In addition to the main electrochemical reactions, others are possible. At the anode, oxygen gas may be evolved by reaction 21. The potential required for this reaction is lower than that for equation 18 and is thermodynamically preferred. Carefully controlled conditions and optimum electrode materials are therefore required to ensure that this reaction does not proceed to a significant extent (Pletcher, 1982).



Other half cell reactions may also occur at the anode. Of interest is the possibility of organic carbon being oxidised directly at the anode surface. Generally this is not expected to be a major factor for many organic molecules because it would mostly require greater potentials than those to produce Cl₂ and the oxidation would not be thermodynamically favoured. However, specific compounds, such as some conjugated aromatics and organic amines may be capable of being partially oxidised at the anode. For example, aromatic compounds can lose an electron from the aromatic ring and activate the molecule to undergo further reactions (Adams, 1969). Such molecules will therefore be more reactive with free chlorine. Non-substituted aliphatic organic molecules are not readily oxidised (Adams, 1969), consequently, the extent of their oxidation will be dependent upon the exact potential of the cell.

At the cathode a significant interference can occur through the formation of hydroxide at the electrode surface (equation 19). This hydroxide will react with magnesium and calcium ions present in seawater (Table 2.1) forming a loose, bulky scale on the electrode surfaces as in equation 22.



To reduce the incidence of this deposit, the flow through the cell must be turbulent, allowing no dead spots for accumulation on surfaces. To remove this deposit, the cell and whole unit is back flushed daily but frequent mechanical removal is also required (Bayliss & Creedon, 1993). Hydrogen and the other gases produced are vented from the electrocatalytic cell.

For effective disinfection, the manufacturer recommends that chlorine levels greater than 150 mg/l (measured in the bulk sewage) be produced from the electrochemical cell (Bayliss & Creedon, 1993). To achieve this level, higher concentrations of free chlorine must be produced close to the anode surface before mixing into the bulk liquid. Consequently, there will exist a transient time during the process when very high levels of free chlorine exist.

In the holding tank, chlorination performs the multiple functions of disinfection and reduction of COD and BOD. Table 6.1 lists the IMO requirements for discharge of sewage in coastal waters.

Table 6.1 IMO Required for Sewage Discharge

Parameter	Permissible mean concentration
Faecal Coliforms	250 CFU/100 ml (MPN) ¹
Total suspended solids	100 mg/l
BOD ₅	50 mg/l

1. CFU is colony forming units and MPN is the most probable number

6.2 Performance of Chlorination in Omnipure Plants on HMAS Hobart

To determine the performance of these OMNIPURE systems on ships of the RAN, the three units on HMAS Hobart were thoroughly tested for compliance with the IMO standards (Table 3.1) and for residual chlorine in the effluent stream. This testing was performed by an independent consulting laboratory. This involved a 10 day sea trial during which system performance was measured using faecal coliforms (FC), total suspended solids (TSS) and BOD₅ and total residual chlorine (TRC). The residual chlorine measurements were done onboard ship immediately after sampling; other samples were returned to the laboratory (Comar, 1993).

A supplementary sampling and analysis was performed to investigate the organohalide content of the effluent. In this study the effluent, also from HMAS Hobart, was analysed for specific organohalides including THMs.

HMAS Hobart has a unique set-up with three identical 12MXS OMNIPURE units, one forward and two aft. The forward unit (No. 1) operates independently serving this part of the ship, while the two aft units work in parallel, with unit No. 3 being the main unit while No. 2 takes only the overflow during peak flows. These two units can be switched to alternating roles. There are continually flushing urinals on HMAS Hobart which provide a dilute sewage. Summaries of the results for this trial are shown in Tables 6.2-6.4.

Table 6.2. Summary of Analyses of HMAS Hobart OMNIPURE Plant, No. 1, Forward Unit (Comar, 1993)

Parameter	Mean	Range	% Failing Standard
Faecal coliforms (CFU/100ml)	35	<20-16,000	29.5
TSS (mg/l)	129.8	8-664	56.8
BOD ₅ (mg/l)	74.2	19-320	72.7
Total Residual Chlorine (mg/l)	55	25-130	NA

Table 6.3. Summary of Analyses of HMAS Hobart OMNIPURE Plant, No. 2, AFT Auxiliary Unit. (Comar, 1993)

Parameter	Mean	Range	% Failing Standard
Faecal Coliforms (CFU/100ml)	7.3	<20-9,000	10.5
TSS (mg/l)	77.1	13-638	36.8
BOD ₅ (mg/l)	56.7	<7-220	60.5
Total Residual Chlorine ¹ (mg/l)	49.7	10-150	NA

Table 6.4. Summary of Analyses of HMAS Hobart OMNIPURE Plant, No. 3, AFT Main Unit. (Comar, 1993).

Parameter	Mean	Range	% Failing Standard
Faecal Coliforms (CFU/100ml)	73.8	<20-16,000	48.5
TSS (mg/l)	145.2	2-800	66.6
BOD ₅ (mg/l)	88.5	21-330	81.8
Total Residual Chlorine ¹ (mg/l)(1)	45.7	8-350	NA

The OMNIPURE units on HMAS Hobart frequently did not perform to the IMO standards for coliforms, TSS and BOD₅. This could indicate that the contact time was too short for sufficient oxidation of organic material and for settling of solids, or that the chlorine concentration was insufficient. The total residual chlorine levels that were measured were for the effluent leaving the effluent holding tank and are a measure of both the free chlorine and combined chlorine concentrations. Consequently, this does

not measure the initial free chlorine and combined chlorine levels after the electrolysis cell. In view of the frequent incidence of effluent samples with high levels of total residual chlorine after the reaction time, it is highly probable that chlorine levels in the cell are initially much higher.

At the current level of chlorination in the OMNIPURE units, the total residual chlorine level being discharged is high compared with other industrial chlorination discharges. Typical chlorine residuals found in other processes are shown in Table 6.5. Generally chlorine gas is dosed into sewage effluent in the range of 1-10 mg/l and much less for cooling waters. Consequently, the total residual chlorine in the effluents from OMNIPURE units on HMAS Hobart is substantially greater than total residual chlorine found in other effluents.

Table 6.5. *Typical Residual Chlorine Discharged From Other Chlorination Processes*

Description	Total Residual Chlorine (mg/l)	Reference
Commercial Spas	1-34	Steininger, 1985
Municipal Sewage Treatment Plants	0.2	Jolley <i>et al.</i> , 1983
Antifouling in Powerplant Cooling	0.2 for 2h/d	Al Hoti <i>et al.</i> , 1988

6.3 Chlorination Products From HMA Ships Fitted With OMNIPURE Units

In OMNIPURE, the high residual chlorine content, along with the initial higher localised concentrations of free chlorine and the contact time of over 30 minutes has the potential to produce many organohalides. A preliminary analysis for organohalides was performed on effluents from these same three OMNIPURE plants. The samples were tested for volatile organochlorides, chloroacetones, chloroanisoles and chlorinated phenols. The chemicals most observed were volatile chlorinated hydrocarbons; only one of 19 chlorinated phenols was identified and no chloroacetone or chloranisoles were observed. The results are shown in Table 6.6.

Table 6.6. *Organohalides in Effluent from OMNIPURE Units*

Organohalide	No. 1 (mg/l)	No. 2 (mg/l)	No. 3 (mg/l)
Bromodichloromethane	0.007	0.013	0.005
Dibromochloromethane	0.019	0.034	0.019
Bromoform	0.059	0.16	0.093
cis-1,2-dichloroethylene	0.004	0.007	0.002
cis-1,3-dichloropropene	ND	0.005	ND
1,4-dichlorobenzene	0.004	ND	0.001
2,6-dichlorophenol	0.04	ND	ND

The THMs observed were consistent with chlorination in the presence of high bromide ion levels which is expected with the high seawater content in the influent (Cooper *et al.*, 1983). These results are higher than some reported values (Singer, 1988; Cooper *et al.*, 1983) and could have resulted from a combination of long contact times of over 30 minutes, or to a high free chlorine to ammonia ratio (ie above break point of chlorination). Plant No. 2 produced the greatest THM concentration and since this plant only handles excess flow, there could be a greater contact time in the holding tank than the others.

Even though the proportion of THM to TOX increases with time, THMs are generally expected to comprise only 9-19% of the TOX (Singer, 1988). Consequently, in this trial, possibly not all of the organohalides in these samples were detected in the above analyses. This is consistent with other observations in that not all organohalides produced are identifiable with current analytical methods, because of the low concentrations and complex structures of individual organohalide compounds. In addition very few brominated compounds were searched for within the effluent samples. Given that the bromide ion concentrations were going to be substantial in this sewage, brominated organic compounds would have been expected. The other organohalide compounds identified, except for 1,4-dichlorobenzene, had not been observed by previous researchers (Table 2.1 and 2.2). Except for 1,4-dichlorobenzene used in 'air fresheners' and probably present in the influent sewage, the exact origin of these compounds is unclear. In addition these organohalide results were found from only one sample. The ship trial of the OMNIPURE system showed how variable the conditions were within the units and as a consequence, organohalide formation would be expected to vary widely.

The OMNIPURE units operating on HMAS Hobart are discharging effluents, high in total residual chlorine, moderately high in THMs and with an unknown portion of organohalides that are not easily characterised. Although each of the HMA Ships with OMNIPURE units are set-up and operated slightly differently (Bayliss & Creedon, 1993), there may be some difference in the organohalide output. However, some generalisations can be made.

- High total residual chlorine levels are expected because the of manufacturer's design for 150 mg/l chlorine production from the electrolysis cell. Whether this residual is made up of free or combined chloride is dependent on the ammonia concentration in the sewage which will vary between ships. However, with sufficient contact time in the holding tank all free chlorine is expected to be reacted and on discharge most of the residual should consist of combined chlorine.
- With the high chlorine dose, high THM production is expected. Because of the high seawater content in the sewage, bromoform is expected to be the dominant THM, followed by dibromochloromethane, bromodichloromethane and with very little if any chloroform. The exact concentrations of these will vary but are expected to be in the µg/l range.

- Given the variable composition of influent sewage and the inconstant chlorination levels and reaction time, all or any of the possible reactions outlined in section 2 can proceed in OMNIPURE systems. However, if only approximately 9-19% of the TOX concentration is caused by THMs then the remainder must be other organohalides. Using the maximum concentration for THMs found on HMAS Hobart of 0.2 mg/l for unit 2 gives the maximum TOX concentration of around 2.3 mg/l.

7. Advisability of Continuing Chlorination

7.1 Physical Factors

OMNIPURE units are consistently failing to produce effluents that meet the IMO sewage discharge standards for BOD₅ and total suspended solids. Only plant No. 2, the auxiliary unit, produced effluents which met the IMO standard for total suspended solids and this is probably due to longer intervals between discharges which results in greater settling of particulates. These high failure rates are occurring concurrently with a high residual oxidant concentration in the effluent. There are two ways of reducing these failure rates, firstly by increasing the initial chlorine concentration or by increasing the reaction time. However, it has been shown that the amount of organohalides produced are proportional to both of these factors. Consequently greater organohalides would be discharged in effluents if either of these were tried. In addition increasing the initial chlorine concentration without increasing the reaction time would result in a greater residual chlorine concentration.

The current RAN DI(N) limit of 20 mg/l for residual oxidant is frequently being exceeded. To reduce the residual oxidant concentration produced in OMNIPURE units to this level would increase the failure rates for BOD₅, faecal coliforms and total suspended solids. Consequently, OMNIPURE units are neither effective in meeting the IMO standards nor are they meeting the DI(N) for residual oxidant and it is unlikely that OMNIPURE units can be made to meet both requirements concurrently.

In effluents from HMAS Hobart's OMNIPURE units we observed a residual oxidant concentration of around 50 ppm, THM concentrations of around 0.1 to 0.2 mg/l and a TOX concentration of up to 2.3 mg/l. The residual oxidant concentration is well above the concentration required to cause toxic effects in many marine species. For example the LC₅₀ levels for many shellfish and fish are in the order of 0.1 mg/l and being exceeded by 500 times. However, much of the residual oxidant will consist of combined oxidant which is often less toxic than free oxidant. Also, residual oxidant will mix with seawater and be diluted fairly rapidly. In addition other degradative pathways as outlined in section 3 will reduce the residual oxidant concentration in the receiving waters. Consequently, as the amount of effluent discharged is small in relation to the volume of the receiving waters, rapid dilution is expected. However,

there could be localised effects being observed at the point of discharge. Young and small fish have been found to be more susceptible to chlorine toxicity than larger species or adults. Considering this, less local disturbance will be experienced if OMNIPURE effluent is discharged away from entrances to estuaries and other breeding areas.

The concentrations of THMs and organohalides will also be subject to dilution. However, their greater persistence in the marine environment and their propensity to be bioaccumulated by living organisms means that dilution may not eliminate toxicological impacts. While the expected contribution from chlorinating ship sewage to the total marine loading of these pollutants is small, these will add to the load already in the receiving waters with an accumulative effect on marine species. Consequently, chlorinating ship sewage is contributing to a growing environmental problem, although, the exact impact of this is dependent on many variables including the concentration of organohalides already present in the receiving waters, the species present in these waters and their density. In addition the major THM expected in the effluent is bromoform which has been shown to be the most toxic THM to marine species. Considering this, discharge of OMNIPURE units should have less environmental impact if carried out further away from shore, where dilution is greatest and biological density and diversity is generally reduced.

Many other technologies exist capable of disinfecting ships sewage to meet the IMO guidelines for sewage discharge. In particular the use of ozone, or ozone and UV, membrane filtration, biological methods, or adoption of collection, holding and transfer processes (CHT). Consequently eliminating chlorination from HMA Ships' sewage treatment would not create a difficult problem.

7.2 Political and Regulatory Factors

In response to available scientific information about the potential toxicity of organohalides, the use of chlorine by various industries is coming under increasing scrutiny, with lobby groups such as Greenpeace mounting organised campaigns aimed at eliminating the use of chlorine. Such lobby groups as Greenpeace are not principally concerned about awaiting definite scientific proof that a process is environmentally harmful. Instead they take a more precautionary approach, which places the onus of proof on the polluter to show that any substance is safe (Ruchel, 1995).

Using this philosophy, Greenpeace has labelled these organohalides as "killer chemicals", is discussing the issue in terms of a "chlorine crisis" and is currently calling for the phase-out of polyvinylchloride polymers, chlorinated pesticides, incineration (which produce dioxins), paper manufacturing using chlorine and dry cleaning fluids using chlorinated solvents. At present marine sanitation of sewage has not been explicitly singled out in this campaign, however, the use of chlorine for

drinking water and sewage disinfection has been (Greenpeace, 1995). Consequently, political pressure for chlorine elimination as a disinfectant is expected to increase.

The OMNIPURE effluent has a high residual oxidant concentration compared to other chlorination processes. In fact OMNIPURE units are discharging effluents with residual oxidants which are approximately 250 times greater than the average municipal sewage plant. This could be an additional reason for marine chlorination of sewage using this technology to be targeted in the future, especially considering that alternatives exist.

Some countries have already independently regulated the discharge of chlorine and organochlorides into marine waters. For example, the US Navy has seen their operations restricted by the EPA and State of Hawaii imposing restrictions on residual oxidant discharge into Pearl Harbour. At present ships docked in Pearl Harbour are only allowed to discharge 0.1 mg/l residual oxidant for 2 hrs per day (Christian *et al.*, 1995). OMNIPURE effluent commonly exceeds this concentration by 500 times.

Consequently, the unrestricted discharge of chlorinated effluents into international waters which is currently occurring may alter in the future. However, this is unlikely to be changed in the short term. Of more immediate concern is the increasing regulation by individual nations to restrict discharge of residual oxidants into their waters. Consequently, RAN may find their operations affected if chlorination of sewage continues.

8. Conclusions and Recommendations

Chlorinating ships' sewage produces effluents which have high residual oxidant levels, around 50 mg/l. At this concentration there could be some localised interference with living organisms. However, rapid dilution and dispersal will limit these effects considerably. In addition chlorination in OMNIPURE units can produce effluents with more than 2 mg/l organohalides and because of their persistence and bioaccumulative characteristic these will ultimately add to the pool of organochloride pollution already present in the environment. The exact biological impact of this organohalide load is not easy to predict but increasing political and regulatory pressure may in the future impinge on the use of chlorination as a method of sanitization.

The amount of residual oxidant that is being discharged commonly exceeds the Defence Instruction (Navy), ie, *DI(N) OPS 19-1 Policy for the Disposal of Shipborne Waste* (Department of Defence, (Navy) 1994) guideline of less than 20 mg/l. Reducing the chlorine residual to this level will either increase the failure rates for BOD₅, faecal coliform and total suspended solids reduction or increase the amount of organohalides present in the discharge. Consequently, the 20 mg/l chlorine residual quoted in this

DI(N) will be difficult to maintain and at the same time meet the IMO guidelines for sewage discharge.

The phase-out schedule for sewage chlorination on RAN ships is strategically appropriate but does not fully address the environmental damage occurring before that time. In view of the environmentally damaging organohalide load in treated sewage, some additional measures should be put in place. One method would be to restrict its discharge to open ocean. For example, it is advisable to alter DI(N) OPS 19-1 to prohibit discharge of OMNIPURE treated sewage in ports and within the Great Barrier Reef Region. An additional step may include early separation of sewage solids with discharge of water using membrane separators. Alternatively, the OMNIPURE units could be removed and the space converted into additional holding tanks to give sufficient storage capacity to allow ships to reach the 12 nm limit required for the discharge of raw sewage.

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REVIEW OF CHLORINE AND ORGANOHALIDES AND THEIR SIGNIFICANCE TO THE ROYAL AUSTRALIAN NAVY

F. John Upsher and Lyn E. Fletcher

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The Royal Australian Navy (RAN) is currently chlorinating ship sewage on some ships prior to discharge. This review was undertaken to assess whether this could pose an unacceptable environmental risk and subsequently be subject to future regulation. It is concluded that chlorinating sewage may pose an environmental risk, however, the level of that risk is unclear. In addition, it is conceivable that further regulation may occur. Moreover, the OMNIPURE units in use by the RAN are not effectively meeting the International Maritime Organisation's regulations for sewage discharge at present. Consequently, it is advisable that alternative sewage treatment systems be adopted.